

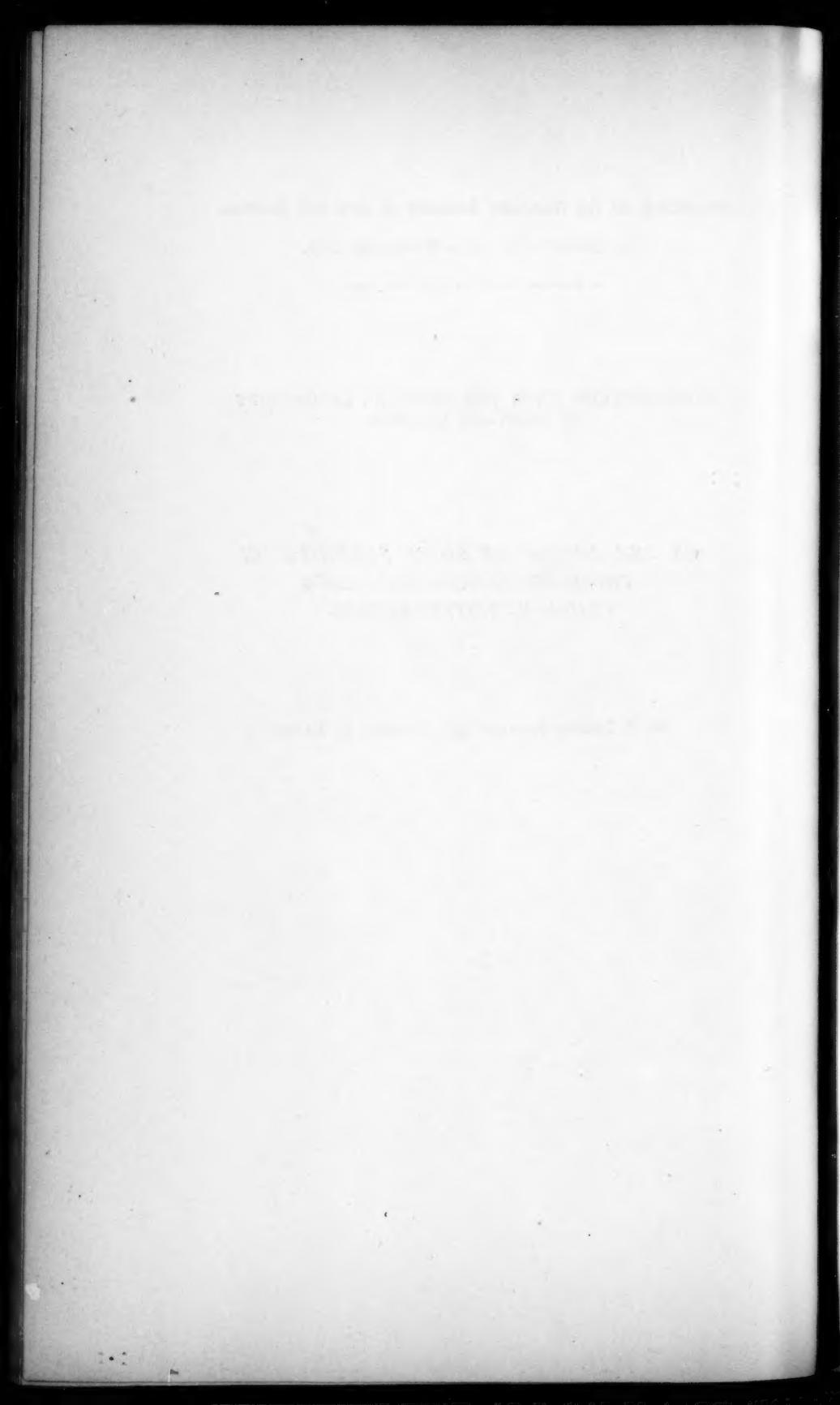
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

*ON THE ACTION OF SODIC SULPHITE ON
TRIBROMDINITROBENZOL AND
TRIBROMTRINITROBENZOL.*

BY C. LORING JACKSON AND RICHARD B. EARLE.



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ON THE ACTION OF SODIC SULPHITE ON TRIBROM-
DINITROBENZOL AND TRIBROMTRINITROBENZOL.

BY C. LORING JACKSON AND RICHARD B. EARLE.

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In the course of an extended study of the action of various reagents on tribromdinitrobenzol ($\text{Br}_3\text{C}_6\text{H}_3\text{NO}_2$) it became of interest to determine whether this substance could be converted into a sulpho-acid by the method of Strecker,* that is, boiling the halogen compound with an aqueous solution of normal sodic sulphite, and experiments in this direction were tried rather early in the work, with negative results. Upon returning to the subject later we did not find any conditions under which an aqueous solution of sodic sulphite acted on tribromdinitrobenzol, but when we substituted alcohol for water as the solvent, we obtained a reaction. This, however, took a different direction from that which we had expected, as under these conditions the sodic sulphite acts as a reducing agent, converting the tribromdinitrobenzol into dibromdinitrobenzol by replacing one of the atoms of bromine by hydrogen. The atom of bromine replaced is the one between the two nitro groups, since the dibromdinitrobenzol formed melted at 117° , which is the melting point of the dibromdinitrobenzol † $\text{Br}_2\text{C}_6\text{H}_3\text{NO}_2$. That the product had this constitution was confirmed by its conversion into the bromanilidodinitrobenzol, which showed the melting point 157° . ‡ Tribromtrinitrobenzol undergoes a similar reduction with an alcoholic solution of normal sodic sulphite, the product being dibromtrinitrobenzol, which can have only this constitution: $\text{Br}_2\text{C}_6\text{H}_3\text{NO}_2$. It is a new substance, and melts at 135° .

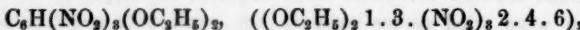
* Ann. Chem. (Liebig), CXLVIII. 90.

† Koerner, Gazz. Chim., 1874, 305.

‡ Jackson and Cohoe, These Proceedings, XXXVI. 75.

In the hope of finding an easier method for making this dibromtrinitrobenzol the action of dibromdinitrobenzol ($\text{Br}_2 1.3 \cdot (\text{NO}_2)_2 4 \cdot 6$) with nitric and sulphuric acids was studied. This gave the desired dibromtrinitrobenzol, but the product was mixed with so large a proportion of tribromdinitrobenzol that the method was not adapted to the preparation of the substance. This tribromdinitrobenzol is a new substance, melting at 150° . There can be no doubt that its constitution is $\text{Br}_3 1.2.3 \cdot (\text{NO}_2)_2 4 \cdot 6$, since it is made by introducing a third atom of bromine into the dibromdinitrobenzol $\text{Br}_2 1.3 \cdot (\text{NO}_2)_2 4 \cdot 6$, and, if this occupied the only other vacant place (5), the product would be the common tribromdinitrobenzol, which melts at 192° . The formation of this tribromdinitrobenzol during this reaction is strictly according to the analogy of the behavior of the tribromdinitrobenzol, which, when boiled with a mixture of fuming nitric and sulphuric acids, gives rise to tribromtrinitrobenzol and tetrabromdinitrobenzol.*

As neither of the new substances just described can be prepared easily on a large scale, we have confined our work on them to the study of the principal action of sodic ethylate on each. This reaction runs in a normal way, giving styphnic diethylether,



with dibromtrinitrobenzol, recognized by its melting point 121° ; and with tribromdinitrobenzol a new bromdinitroresorcine monoethylether melting at 78° . The subject did not promise to be of sufficient interest to make it worth while to study the secondary products of these reactions.

EXPERIMENTAL PART.

Action of Sodic Sulphite in Alcoholic Solution on Tribromdinitrobenzol.

Five grams of symmetrical tribromdinitrobenzol ($\text{Br}_3 1.2.3 \cdot (\text{NO}_2)_2 2 \cdot 4$) were dissolved in 70 c.c. of alcohol mixed with 20 c.c. of benzol, five grams of normal sodic sulphite added, and the mixture boiled for five hours in a flask with a return condenser. The red liquid thus obtained was filtered from the insoluble portion, evaporated to dryness, and the residue washed with water, until the yellow color was removed. The part insoluble in water was then recrystallized from alcohol with the aid of bone-black, until it showed the constant melting point 117° . This melting point indicated that it was Koerner's dibromdinitrobenzol †

* Jackson and Wing, These Proceedings, XXII, 139

† Gazz. Chim., 1874, 305.

$(Br_2 1.3, (NO_2)_2 4.6.)$, and this was confirmed by treating it with aniline in the cold, when it was converted into the bromanilidodinitrobenzol, * $C_6H_2Br(C_6H_5NH)(NO_2)_2$, recognized by its melting point 157° . For greater certainty the dibromdinitrobenzol was dried at 100° , and analyzed with the following results: —

- I. 0.3277 gram of the substance gave 24.6 c.c. of nitrogen at a temperature of $18^\circ.5$ and a pressure of 760.3 mm.
- II. 0.3195 gram of the substance gave by the method of Carius 0.3707 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NO_2)_2$	Found.	
		I.	II.
Nitrogen	8.59	8.65	
Bromine	49.38		49.08

The sodic sulphite, therefore, has removed the atom of bromine standing between the two nitro groups in the tribromdinitrobenzol, and replaced it by hydrogen.

That this was not the only action of the sodic sulphite was shown by the marked yellow color of the products of the reaction. The yellow substance was soluble in water, but, in spite of its strong color, was present in such small quantity that we could not isolate it from the other substances soluble in water, which consisted of sodic bromide and unaltered sodic sulphite. It was undoubtedly the sodium salt of a phenol formed by a secondary reaction.

Action of Sodic Sulphite in Alcoholic Solution on Tribromtrinitrobenzol.

Ten grams of symmetrical tribromtrinitrobenzol $(Br_2 1.3.5. (NO_2)_2 2.4.6)$ were dissolved in 120 c.c. of common alcohol with the assistance of 30 c.c. of benzol, ten grams of normal sodic sulphite added, and the mixture boiled for four hours in a flask fitted with a return condenser. The reaction seemed to run as in the case of the tribromdinitrobenzol, except that it took place more easily, since the red color appeared more quickly. The red solution was filtered, the filtrate evaporated to dryness, and the residue washed with water, after which it was recrystallized from a mixture of alcohol and benzol with the assistance of bone-black, until it showed the constant melting point 135° , when it was dried at 100° , and analyzed with the following results: —

* Jackson and Cohoe, These Proceedings, XXXVI. 75.

I. 0.2884 gram of the substance gave 25.1 c.c. of nitrogen at a temperature of 25° and a pressure of 753.3 mm.
 II. 0.2887 gram of the substance gave by the method of Carius 0.2910 gram of argentic bromide.

	Calculated for $C_6HBr_2(NO_2)_3$	Found.	
	I.	II.	
Nitrogen	11.36	11.65	
Bromine	43.10		42.89

The substance is, therefore, dibromtrinitrobenzol (Br_2 1. 3. (NO_2)₃ 2. 4. 6.), formed by the replacement of one atom of bromine in the tribromtrinitrobenzol by hydrogen, and the sodic sulphite has behaved like a reducing agent in this case just as it did with the tribromdinitrobenzol.

Properties of Metadibrom-s-trinitrobenzol.—It crystallizes from benzol—or better, a mixture of benzol and ligroin—in broad prisms terminated by two planes at a slightly acute angle to each other, or in slender, blunt-ended prisms, or in rhombic crystals. It has a pale yellow color with a slight greenish tinge, and melts at 135°. It is freely soluble in benzol or ether; soluble in chloroform, acetone, or cold alcohol, freely soluble in hot alcohol; slightly soluble in hot ligroin; insoluble in water. The best solvent for it is a mixture of alcohol and benzol, or of benzol and ligroin; strong hydrochloric or sulphuric acid has no action on it, either hot or cold. Strong nitric acid does not dissolve it in the cold, but forms a yellow solution with it when hot, which deposits the unaltered substance on cooling. Sodic hydrate solution gives a pale yellow solution when hot; no perceptible action when cold. Alcoholic sodic hydrate gives a deep red color.

The aqueous wash waters obtained in the preparation of dibromtrinitrobenzol by this process, although showing a strong red color, contained so little organic matter that we did not succeed in isolating any new compound from them. The residue left on evaporating them consisted chiefly of sodic bromide and unaltered sodic sulphite.

Preparation of Dibromtrinitrobenzol from Dibromdinitrobenzol.

In the hope of finding an easier method of preparing the dibromtrinitrobenzol we next tried to make it from dibromdinitrobenzol. The dibromdinitrobenzol was made by the method of Jackson and Cohoe,* which, however, we modified somewhat in converting the bromacetanilid

* These Proceedings, XXXVI. 77.

into dibromacetanilid, — the monobromacetanilid was mixed with enough glacial acetic acid to convert it into a semi-liquid mass, to which the calculated amount of bromine was added from a burette. It was then warmed on the steam-bath, until it was transformed into a clear, dark-red liquid, which was poured into water, filtered, and the precipitate ground in a mortar with a solution of sodic hydrate to remove the excess of bromine. The dibromdinitrobenzol used for our work was recrystallized until it showed the correct melting point 117°.

To convert the dibromdinitrobenzol into dibromtrinitrobenzol we proceeded as follows. Twenty grams of dibromdinitrobenzol were added to 500 c.c. of fuming nitric acid of specific gravity 1.50 and 200 c.c. of sulphuric acid of specific gravity 1.86, and the mixture was boiled violently for about three hours in a flask closed with a porcelain crucible. Toward the close of the operation a reddish oil separated, after which the process was continued only so long as the liquid boiled freely, since decomposition and darkening of the color resulted from too long continued boiling. After the mixture had been boiled for a sufficiently long time, it was allowed to cool, poured into ice water, and filtered. The precipitate was recrystallized from a mixture of alcohol and benzol, until it showed a constant melting point, but, as this stood at 150°, the substance was not the expected dibromtrinitrobenzol, which melts at 135°. On examining the mother liquors from this substance, however, we found the dibromtrinitrobenzol, which, after purification by crystallization from a mixture of benzol and ligroin, was recognized by its melting point 135°, and the following analysis of the substance dried at 100°: —

0.2174 gram of the substance gave by the method of Carius 0.2203 gram of argentic bromide.

	Calculated for $C_6HBr_3(NO_3)_2$	Found.
Bromine	43.10	43.10

The dibromtrinitrobenzol is therefore formed by this process, but so much of the other product melting at 150° is formed at the same time that this is not a convenient method of preparing it, and the dibromtrinitrobenzol remains a not easily accessible substance.

Tribromdinitrobenzol, $C_6HBr_3(NO_3)_2$. (Br₃ 1. 2. 3. (NO₃)₂ 4. 6.).

The substance melting at 150°, prepared by the action of nitric acid and sulphuric acid on dibromdinitrobenzol as described in the preceding section, was dried at 100°, and analyzed with the following results: —

I. 0.2973 gram of substance gave according to the method of Carius 0.4138 gram of argentic bromide.

II. 0.2987 gram of substance gave 0.4150 gram of argentic bromide.

	Calculated for $C_6HBr_3(NO_2)_3$.	Found.	
	I.	II.	
Bromine	59.26	59.24	59.13

The substance is, therefore, a tribromdinitrobenzol, and its appearance is not unexpected, since J. F. Wing and one of us* found that tetrabromdinitrobenzol was always formed during the preparation of tribromtrinitrobenzol from tribromdinitrobenzol. There can be no doubt about the constitution of this tribromdinitrobenzol, because it is made from the dibromdinitrobenzol (Br_2 1. 3. (NO_2)₂ 4. 6) by the introduction of an atom of bromine, which can enter only in two places,—between the nitro groups, or between the atoms of bromine. If the substitution takes place between the nitro groups, there must be formed symmetrical tribromdinitrobenzol, which melts at 192°; there is left, therefore, for our substance melting at 150° only the constitution Br_3 1. 2. 3. (NO_2)₂ 4. 6.

Properties of the 1. 2. 3. Tribrom-4. 6. dinitrobenzol.—Yellowish white rectangular plates bevelled on the sides, when crystallized from a mixture of alcohol and benzol. Melting point 150°. It is freely soluble in benzol, or ether; soluble in chloroform, glacial acetic acid, or acetone; soluble in cold alcohol, freely soluble in hot alcohol; slightly soluble in cold ligroin, soluble in hot; insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Strong hydrochloric or sulphuric acid gives no visible action hot or cold. Strong nitric acid appears not to act in the cold, but dissolves it when hot, depositing the unaltered substance as it cools. A solution of sodic hydrate does not act on it apparently either hot or cold, but in presence of alcohol gives a light yellow color.

Action of Sodic Ethylate on Dibromtrinitrobenzol.

1.5 grams of dibromtrinitrobenzol (Br_2 1. 3. (NO_2)₂ 4. 6) were dissolved in 15 c.c. of benzol, and mixed with sodic ethylate in the proportion of three molecules of the ethylate to each molecule of the dibrom compound. The sodic ethylate was prepared by adding the calculated amount of sodium to 30 c.c. of absolute alcohol. The liquid at once took on an intense red color, and became turbid. To make sure of completing the reaction the mixture was allowed to stand for twelve hours at ordinary temperature in a cork flask, after which it was filtered, and the

* These Proceedings, XXIII. 139.

filtrate allowed to evaporate spontaneously ; the residue was washed with water until the washings were colorless, and then recrystallized from alcohol until it showed a constant melting point, which was found to be 121°. The melting point of styphnic ethylether,



is given as 120°.5, and it is described as forming long plates, which quickly turn orange-brown in the light ; our substance crystallized in prisms connected by their longer sides, and turned brown by exposure to the light. It contained no bromine. There can be no doubt, therefore, that the two bodies are identical, and that this styphnic ether formed by replacing each bromine by an ethoxyl group is the principal product of the reaction. It was not, however, the only product of the action of sodic ethylate on dibromtrinitrobenzol, as the reaction product insoluble in the organic solvents but soluble in water gave tests for nitrite as well as bromide, and the aqueous washings were colored ; but the amount of these secondary products was so small that they could not have been studied without preparing the mother substance on a very large scale, and the importance of the subject did not warrant the great expenditure of time which would have been necessary for this purpose.

Action of Sodic Ethylate on Adjacent Tribromdinitrobenzol.

Seven grams of the tribromdinitrobenzol ($Br_3 1.2.3 \cdot (NO_2)_3 4.6$) were dissolved in 70 c.c. of benzol, and mixed with sodic ethylate in the proportion of three molecules of the ethylate to each molecule of the tribromdinitrobenzol. The sodic ethylate was prepared by adding the calculated amount of sodium to 70 c.c. of absolute alcohol. A deep red turbid solution was formed immediately, which was allowed to stand in a corked flask at ordinary temperatures for two days, and then filtered, the filtrate allowed to evaporate spontaneously, and the residue washed with water, until the washings were colorless. The portion insoluble in water after recrystallization from alcohol showed the constant melting point 58°, and crystallized in long white needles turning yellow in sunlight, but was formed in such small quantity that there was not enough for analysis ; we, therefore, sought the principal product of the reaction in the portion soluble in water. The precipitate formed during the action of the sodic ethylate was dissolved in water, and mixed with the wash waters, which had previously been concentrated to a convenient bulk. The solution was then acidified with acetic acid, which threw down a black tarry precipitate. This was filtered out, washed, suspended in water, and dissolved by adding sodic hydrate to neutralization ;

the solution was filtered, and treated with baric chloride, which produced at once a mass of shining yellow needles. These were filtered out, washed with water, and recrystallized several times from alcohol; after which they were dried at 100°, and analyzed with the following results:

I. 0.3636 gram of the substance gave 0.1108 gram of baric sulphate.
 II. 0.3071 gram of the substance gave 21.2 c.c. of nitrogen at a temperature of 22°.5 and a pressure of 765 mm. The substance was mixed with a large excess of a mixture of eight parts of fused plumbic chromate with one of potassic dichromate. It was necessary to heat very gradually to avoid too rapid an evolution of the nitrogen.

	Calculated for [C ₆ HBr(NO ₂) ₃ (OC ₂ H ₅)O] ₂ Ba.	Found
	I.	II.
Barium	18.33	17.91
Nitrogen	7.47	7.86

The substance is, therefore, the barium salt of a bromdinitroethoxyphenol. We have not determined the constitution of this substance experimentally, but there can be little doubt that it is a derivative of resorcine, as the two bromine atoms in the meta position to each other are also in the para and ortho positions to the nitro groups, and this has been shown to be the position most favorable to replacement; whereas the third atom of bromine, which is in the meta position to the two nitro groups, would be replaced with difficulty according to all previous work on this subject; we have no hesitation, therefore, in calling this substance the bromdinitromonoethyl ether of resorcine.

Properties of the Barium Salt.—It crystallizes from alcohol in fine yellow needles. It is nearly insoluble in water, whether hot or cold, but soluble in alcohol. It is stable at 100°, but if heated suddenly to a high temperature it explodes. Acetic acid does not decompose it.

The free bromdinitromonoethyl ether of resorcine was obtained by heating the barium salt with an acid; after crystallization from alcohol it melted constant at 78°. It forms long white feathery needles, which turn yellow on standing.

The experiments just described make it highly probable that the substance melting at 58° and insoluble in water is the bromdinitroresorcine-diethyl ether. There were also other products of the reaction, as the soluble salts obtained gave a test for nitrite as well as for bromide, but they were formed in such small quantity that it did not seem to us worth while to undertake the study of them.

